A Systems Approach to the Service Life Prediction Problem for Coating Systems

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INTRODUCTION

Over the last two decades, the organic coatings industry has undergone rapid technological and structural changes. These changes have been largely forged by legislative actions such as restrictions pertaining to hazardous chemicals, toxic effluents, waste disposal, and volatile organic compounds. Further changes have been induced by competitive and consumer pressures to produce environmentally and user friendly coatings without sacrificing ease of application, initial appearance, or, most importantly, significantly reducing the expected **service life** (SL) of the coating systems. One consequence of these changes has been the gradual displacement of almost all commercially-important, well-established maintenance coatings (largely high-solvent coatings) by newer systems; the formulation and application of which are often based on different chemistries and technologies.

Unlike the coatings which have and are being displaced, however, these new coatings have little or no performance histories and, at present, the generation of a reliable performance history for a new coating requires an extensive in-service or outdoor exposure program which normally takes between five and ten years to complete. Attempts at avoiding this task and, at the same time, minimizing the risks associated with introducing into the marketplace a poorly performing coating through, for example, the use of sophisticated electrochemical measurements, have had limited success. Alternatively, creating a performance history from in-service exposure results requires long exposure times and provides service life estimates of limited utility and reproducibility since the weather never exactly repeats itself [Burroughs[1]; Climate Research Committee[2]].

The coatings industry, therefore, is faced with a dilemma in that the only means for generating timely exposure results is through the use of laboratory tests. Unfortunately, current laboratory tests are, and have historically been, viewed with suspicion within the coatings industry as evidenced by remarks made by the following researchers: Reinhart[3]; Nowacki[4]; Steig[5]; Kamal[6]; Quackenbos and Samuels[7]; Hoffmann and Saracz[8]; Alumbaugh and Hearst[9]; Ellinger[10]; Campbell et al.[11]; Lindberg[12]; Leidheiser[13]; Yaseen and Raju[14]; Chandler and Bayliss[15]; Funke et al.[16]; Cutrone and Moulton[17]; Simms[18]; Masters[19]; Wicks[20]; Skerry et al..[21]; Himics and Pineiro[22].

This lack of confidence in laboratory results, however, is not shared by all industries. For example, the electronics, medical, aeronautical, and nuclear industries have long since made the transition from an overwhelming dependence on long-term in-service tests to a heavy reliance on

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laboratory results. This reliance on laboratory results has greatly reduced the time required to introduce new products into the marketplace and, as a consequence, has greatly increased the competitiveness of these industries. The transition to dependence on laboratory results was greatly facilitated by the service life prediction methodology called reliability theory and life testing analyses (hereinafter, called the reliability-based approach). Unlike the current methodology, the reliability-based methodology is very systematic; has a strong theoretical and scientific basis; and is capable of generating quantitative service life estimates for a coating system exposed in its intended service environment as demonstrated by Tait[23], Tait et al..[24], and Martin et al..[25-27].

The objectives of this paper are to compare the current and reliability-based methodologies and to identify changes required in the current methodology which would have to be implemented in order to undertake a reliability-based methodology.

SOURCES OF SERVICE LIFE DATA

Regardless of the material, product or system, quantitative service life data can only be generated from three sources: 1) **accelerated laboratory exposures**, 2) **outdoor exposures**, and 3) **fundamental mechanistic studies**[28]. Each of these sources possesses both unique and common features and attributes and, thus, each source is equally important in providing data for making service life prediction estimates. For example, exposure variables in both accelerated laboratory and fundamental mechanistic studies can be readily controlled; whereas, it is not possible to control any weathering variable in an outdoor exposure experiment. The ability to control the intensity of the exposure variables provides both accelerated laboratory and fundamental mechanistic studies with the ability of generating information about the underlying failure mechanisms causing a coating system to degrade in a timely manner. Outdoor exposure experiments, on the other hand, normally require long exposure times to generate results, but, at the same time, provide valuable information on the dominant failure modes and failure times. The experimental designs for these three data sources are also different. Fundamental mechanistic studies are designed to extract extensive amounts of information about the underlying chemical and physical mechanisms causing a coating system to fail; whereas accelerated laboratory and outdoor exposures are usually designed to determine a coating systems response when subjected to a specified stress regime.

Since the type of SL data sources is limited, much thought and effort has to be given in assigning the mission, in designing experiments, and in analyzing the resulting data for each of the data sources. Ideally, the output from each of these data sources should be quantitative and directly comparable with the output from the other two sources. This can be achieved if all three data sources use the same quantitative descriptors in characterizing a coating system, the exposure environment, and material degradation.

In the following sections, the current and proposed reliability-based methodologies are compared with respect to their mission statements, assignments, and how they satisfy the above stated issues. In making this comparison, however, it should be recognized that the current service life methodology was implemented prior to the recognition of these issues and a long time before the computational and theoretical tools required to accomplish these tasks were available.

CURRENT SERVICE LIFE PREDICTION METHODOLOGY

The current service life methodology dates back to the early 1900's with the construction of several outdoor exposure sites[29] and the fabrication of crude, by todays standards, weathering devices[30-33]. The underlying philosophy for the current methodology is rather simple—design an accelerated aging experiment which captures the balance of exposure conditions occurring outdoors[10, 34]; that is, laboratory experiments should be designed to duplicate the exposure results obtained outdoors. This goal will be achieved whenever a laboratory exposure test has been designed which consistently achieves a high correlation with similarly exposed panels exposed outdoors. So far, no such laboratory exposure test has met this goal.

A schematic depicting the test strategy for the current methodology is depicted in Fig. 1. As can be seen from this figure, fundamental mechanistic studies do not play any role in this methodology. Instead, accelerated aging tests are iteratively designed to generate results which correlate with those generated outdoors.

The validity of this methodology depends on the validity of three implicit premises. These premises are as follows:

Premise 1: The performance of a coating system can be assessed using one, or at most three replicates;

Premise 2: The results from outdoor exposure experiments are the de facto standard to which the results from any laboratory-based experiment must duplicate (correlate); and

Premise 3: The results from the successful laboratory experiment should correlate with results from any outdoor experiment.

As discussed in the next section, the validity of all three premises has no support in the literature. Particularly important is the failure of the second premise, since if can be shown that the weather does not cycle over any time scale, then the validity of the current methodology is dubious, since outdoor exposure results are used as the performance standard to which laboratory exposure results must compare.

PROPOSED RELIABILITY-BASED SERVICE LIFE PREDICTION METHODOLOGY

Unlike the current service life prediction methodology, the proposed reliability-based methodology has a long and successful history for predicting the service life of a wide variety of products in a large number of industries[35-36]. Moreover, this methodology has a strong and ever evolving theoretical base and heavily depends on the output from fundamental mechanistic studies to improve the precision of the service life estimates.

A schematic of the reliability-based methodology test strategy is depicted in Fig. 2. The underlying philosophy in a reliability-based methodology is that the output from all three sources of service life data quantitative and, thus, comparable. Several aspects of this methodology should be noted. First, laboratory tests are experimentally designed to determine the response of a coating system over the range of exposure and operating conditions that the coating system is expected to encounter in-service. Thus, as discussed below, laboratory experiments are no longer assigned the impossible mission of trying to simulate outdoor exposure environments. Outdoor exposure experiments, on the other hand, are viewed as just another laboratory experiment, albeit one in which neither the weather nor individual weathering factors can be controlled. Instead, individual weathering factors must be monitored in the same manner that these factors are characterized in the laboratory. The results from both outdoor and laboratory exposure results are related to each other through a cumulative damage model (depicted by the computer in Fig. 2) , a mathematical model which accounts for the irreversible accumulation of damage occurring throughout the life of a coating system which ultimately leads to its failure or maintenance. Cumulative damage models for corrosion have still not been developed; but several cumulative damage models for loss-of-appearance have been proposed[37].

In the sections which follow, various aspects of the service life prediction problem for coatings are discussed and citations are given to the reliability literature which address these issues.

Multiple Failure Modes and Multiple Causes of Failure

The service life of a coated product occurs whenever the first of many possible critical performance values is exceeded. For coating systems, critical performance characteristics include those associated with either a loss of protection , a loss of appearance or both. Common loss of protection and loss of appearance failure modes include corrosion, cracking, chalking, and color change (see Fig. 3). The dominant failure mode[38], the failure mode that occurs first or most frequently in a given exposure environment, often changes from one exposure environment to another. Thus, for example, the dominant failure mode in Phoenix, AZ may be quite different from the dominant failure mode in Miami, FL.

Failure of a coated product can often be assigned to one or more faults, often called **root faults.** Examples of root faults include variables related to the exposure environment, the materials for which the product is comprised, material processing, application variables, and the design of the coated product. The actual cause of failure, however, is attributable to a basic **fault(s)** (see Fig 4). Both root and basic faults may differ from one failure mode to another and even can be different for the same failure mode arising from different root faults. Clearly, if the root fault is known, this knowledge would greatly simplify the discovery of the basic fault, since the number of basic faults which would need to be investigated would be greatly reduced. Moreover, once the basic fault has been identified, it is often a simple matter to correct the root fault and, thereby, increase or improve the service life of the product. The service life of this "improved" product will now be limited by a new basic fault. Hence, the investigation process starts anew.

Making a connection between the dominant failure mode and a root or basic fault is seldom an easy task since it requires the elucidation of one or more intermediate physical, chemical, or physical and chemical steps. If the steps are known at a fundamental mechanistic level, then this linkage is completely understood and can be described in terms of the **degradation kinetics**. Bauer et al..[39-44] and Gerlock et al..[45], for example, have made great advances in elucidating the photodegradation mechanisms for clear coatings. Unfortunately, for most commercially important products, and in particular maintenance coatings, our knowledge of the degradation mechanisms is seldom complete. This is particularly true for corrosion processes. Consequently, the linkage between a failure mode and root faults must be empirically described through **cause-and-effect** or **dose-response relationships**; such a linkage is best described by a gray box (see Figure 5); that is, our knowledge of the underlying chemical and physical failure mechanism is not completely elucidated, although dose-response knowledge is readily available.

The reliability-based methodology uses fault tree analyses[46-49], experimental designs[36], and mathematical analysis tools[36] for discriminating among multiple response (failure modes) and independent variables for identifying and ranking the relative importance of different failure modes and faults in limiting the service life of a product.

High Variability in Service Lives of Nominally Identical Products Simultaneously Exposed in the Same Service Environment

The degradation of a coating system over time, and thus its performance, is usually monitored through changes of variables associated with its appearance and its ability to protect a substrate from corrosion. (Hereinafter, called **performance characteristics**). Associated with each performance characteristic is a maximum or minimum **critical value, $\mathbf{h}_{crit}$,** above or below which the coating system is said to have failed (see fig. 6)[23-27, 50]. The critical performance value assigned to a product often varies from one application to another. For example, the critical value for the corrosion of a car is often much less than the critical value for the corrosion of a steel bridge. Fortunately, the assignment of a critical value does not affect the method for analysis of the data.

Prior to the initiation of degradation, a coated product often displays no observable degradation. This time period is called an **induction time** (denoted by t_o in fig. 6). After this induction time, the coated panel begins to monotonically degrade and ultimately fail as soon as the first (earliest) performance characteristic exceeds its critical value, h_c. Such failures are called **out-of-tolerance** or **drift-type failures**[51] and are the most common failure mode for coatings exposed in the field. A much less common type of failure for coating systems exposed in the field is a **catastrophic** or **instantaneous failure** in which a coating system undergoes a rapid change from an unfailed to a failed state. Examples of instantaneous failures include the spalling of a coating resulting from the impact of a projectile[52-53], the etching of a clear coating resulting from acid deposition[54], and flash corrosion resulting from contamination of a coated surface. The **time-to-failure**, t, of a coating system is the minimum time after a coating is applied until a critical performance characteristic exceeds its critical value (fig. 6).

It is quite common in life testing that a critical performance characteristic for a product is not exceeded during exposure; that is, the rate of degradation is so slow that the panel is not considered to have failed prior to the termination of the experiment. The time-to-failure for such panels is said to be **censored.** Censoring can also be caused by damage during handling, loss in shipment, or removal of a panel from an experiment in order to destructively analyze the degradation products (see discussion in reference 36). Due to the commonness of censoring in service life prediction experiments, any proposed service life prediction methodology should be capable of estimating the service life of a product in which some of the service life data is censored.

Censored data often arise when a number of nominally identical specimens are placed on exposure at the same time and the times-to-failure for each of these specimens are tracked. In such an experiment, it becomes quickly evident that the degradation of some of these panels is much faster than that of the other panels; i.e., the degradation of these nominal identical panels displays large temporal variation. An example of the high temporal variability in loss-of-protection response of nominally identical coated panels, see Fig. 7 which show blister area results for 24 replicate specimens were immersed in a 5% salt solution for 6000 h (see Fig. 7)[27]. In this experiment, the first panel started to degrade through cathodic delamination after approximately 1000 h of immersion, while 6 of the 30 panels displayed no signs of degradation after 6000 h of immersion. Thus, the performance of these nominally identical specimens ranged from a poorly performing (time-to-failure less than 1000 h) to a well-performing coating system (time-to-failure greater than 6000 h). Such large temporal variability in the performance of nominally identical coated specimens has been observed by many researchers[23-27, 55-57].

When a coating system is placed on exposure, a number of performance characteristics may change simultaneously. For example, performance characteristics related to loss of protection and appearance may change simultaneously[58]. Each performance characteristic, therefore, effectively competes with the others in causing a coating system to fail (often termed **competing risks**[59]). The failure mode which usually "wins out" is called the **dominant failure mode** for a given exposure environment. The dominant failure mode may change with a slight change in the initial properties of a coating or in the intensity of some of the weathering factors[38, 60]. For example, the dominant failure mode for a coating system exposed in a semi-desert environment like Arizona is often associated with a loss of appearance due to the high spectral ultraviolet irradiance; whereas, the dominant failure mode for the same coating system exposed in Florida may be associated with a loss of protection, which is attributable to the long time of wetness associated with semi-tropical environments.

The high variability in service life data, the presence of censored times-to-failure, and the effects of competing risks on the failure of a coating system are common to almost all materials, components, and systems (see, for example, the citations in reference 36). Reliability theory and life testing analyses has developed an extensive theoretical base for dealing with these problems.

Non-Cyclic Behavior of the Weather over All Time Scales

The weather and individual factors comprising the weather (e.g., spectral ultraviolet radiation, relative humidity, temperature, SO_x, NO_x, O_3, and NaCl) display both high spatial and temporal (diurnal, seasonal, and annual) variability. A key question which must be addressed is whether the weather, or any factor comprising the weather, displays any cyclic behavior over any time scale at a given location. This question must be addressed since a basis premise of the current service life prediction methodology is that such a cyclic behavior exists. If a cyclic pattern doesn't exist, then it is not possible for the current service life prediction methodology to ever generate any quantitative estimates of the service life of a coating system.

This question can be addressed in two ways. First, a determination can be made as to whether any weathering factor exhibits cyclic behavior over any time scale; and, secondly, whether the degradation response of nominally identical specimens exposed in the same exposure environment exhibit reproducible results.

The first question has been addressed[1-2] , and it is now commonly accepted, that that neither the weather nor individual factors comprising the weather cycle over any time scale. This is demonstrated in Fig. 8 for ultraviolet radiation where it can be seen the ultraviolet radiation dos for Rockville, MD remained relatively constant during the 1970's, increased approximately 30% during the 1980's, and precipitously dropped during the early 1990's as a result of volcanic activity. Other examples of non-cyclic behavior of the weathering factors also exist[37].

The reproducibility of weathering experiments has also been investigated by a number of researchers. From these studies, it is known that the observed failure mode for nominally identical specimens often changes from one environment to another[61] and that the rankings of outdoor exposure results do not agree for coated specimens exposed 1) at the same site and at the same time of year, but in different years[62] 2) at the same site, but at different times[5, 10, 12, 34, 62-71] 3) at the same site, same year, and the same time of year, but for different durations[8], and 4) at different sites, but at the same time of the same year[72-28, 5-6, 8, 61, 65-66]. **In fact, no study was found claiming that outdoor exposure results are reproducible.**

Thus, one of the main difficulties in relating laboratory and field results will be in characterizing outdoor weathering histories in a manner that is identical to the way these factors are characterized in the laboratory. Initial efforts in quantifying outdoor weathering factors have been outlined[37].

Quantification of Coating System Degradation

Over the last two decades, significant advances have been made in quantifying both appearance and protective degradation. This is particularly true for laboratory measurements. Examples of advances in appearance measurements at the microscopic and molecular level include infrared spectroscopy[43, 49, 79], x-ray photoelectron spectroscopy[80], electron spin resonance[45], and ATR spectroscopy[81]. Improvements in macroscopic appearance measurements have largely revolved around the computerization of existing optical appearance measurements[82].

Examples of advances in corrosion protection measurements at the microscopic level include chemical property measurements of coating system degradation using Fourier transform infrared spectroscopy[83-84], changes in the electrochemical properties using AC impedance spectroscopy[24,85-86], and changes in the internal mechanical stress properties in a coating system as it ages[87-90]. Improvement in macroscopic corrosion protection measurements include imaging corrosion products or blistered areas using visible or thermographic cameras linked to a computer image processor[91-95] and along with a wide variety of other[96].

Although significant advances have been made in the metrology of microscopic and analytical degradation measurements, macroscopic loss of protection degradation measurements are still too often evaluated using visual standards. In order to make quantitative service life estimates, visual standards will have to be replaced with quantitative measurements like those provided by computer image processing.

Storage, Retrieval, and Analysis of Data

Coating manufacturers routinely collect and store large amounts of data during the manufacture and testing of their coatings. Correspondingly, many coating end-users require data which will convince them that a candidate coating will perform in their application. Formulation, processing, and application variables often affect the service life of a coating system and, therefore, this information should be available for refining the service life estimates for a coating system. This data would be most accessible if it were stored in an electronic format[97]

Computerized databases have enjoyed widespread acceptance in the chemical[98-99], medical[100-102] and aerospace[103] industries. Also, the development of computerized databases has been identified by Ambler[104] and others as a national economic priority. Computerized databases quickly become the repository for the collective institutional knowledge about complex systems. This knowledge can be queried to discover interrelationships among variables[105-106] and, thus, databases eventually become inexpensive adjuncts to physical experimentation.

If the full potential of computerized coating databases is to be achieved, however, several key issues must be addressed including:

1) Standardization of the terminology used in describing coatings, substrates, and defects.
2) Selection and standardization of variables for identifying and tracking the degradation of a coating system.
3) Identification of reliable methods for quantifying coating system degradation.
4) Development of a strategy for ensuring the accuracy of stored data[107].
5) Storage of data in a format which is easily transportable -- that is, a format which is not inextricably linked to anyone computer software/ hardware system.

SUMMARY

Implementation of a reliability-based methodology will require changes in all elements of the current durability methodology. These include 1) more systematic characterization of the initial properties of a coating system, 2) quantitative characterization of each of the weathering factors comprising the in-service environment, 3) quantification of macroscopic degradation and relating these measurements to microscopic degradation measurements, 4) utilization of experimental design techniques in planning and executing short-term laboratory experiments, and 5) development of computerized techniques for storing, retrieving, and analyzing collected data. These changes are necessitated because of the current methodology's inability to make service life estimates; while the conversion to a reliability-based methodology will be justified in view of the greater reliability and quantitative nature of the service life estimates.

The greatest changes in making the conversion from the current service life prediction methodology to a reliability-based methodology, however, will occur in the missions assigned to short-term laboratory based and long-term in-service experiments; the mission of fundamental mechanistic studies remains essentially unchanged except that there may be more emphasis on failure analyses. In a reliability-based methodology, long-term in-service experiments are viewed just like a laboratory-based experiment, albeit one in which individual weathering factors cannot be controlled. Instead, individual weathering factors are characterized in the same manner as they are in the laboratory and the results from field exposure experiments are related to laboratory experiment through cumulative damage models. Laboratory-based experiments, on the other hand, are systematically designed to identify and isolate variables affecting the service life of a coating system. This is accomplished through the implementation of well-known experimental designs. The results from the laboratory and outdoor exposure experiments can be stored in a computerized database for future retrieval and analysis. This becomes feasible if all of the collected data is quantitative in nature and comparable from the macroscopic to the sub-macroscopic levels. The power of computerized databases is that it allows the researcher to query the database for relationships which were not previously recognized without conducting the experiment.

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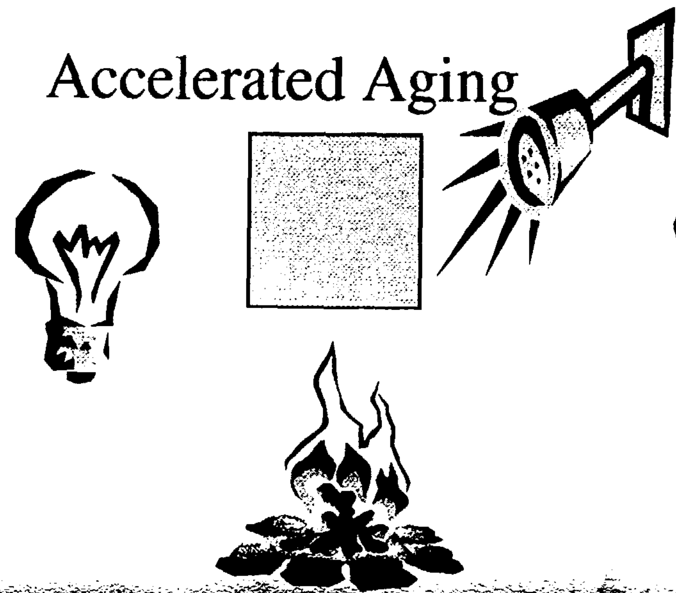
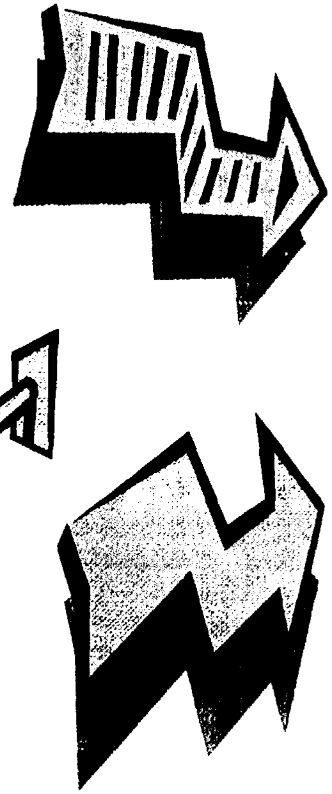
CURRENT SLP METHODOLOGY

Outdoors

Accelerated Aging





Make Comparison
Outdoor vs.
Accelerated Aging

No Correlation;
Adjust Accelerated
Aging Factors

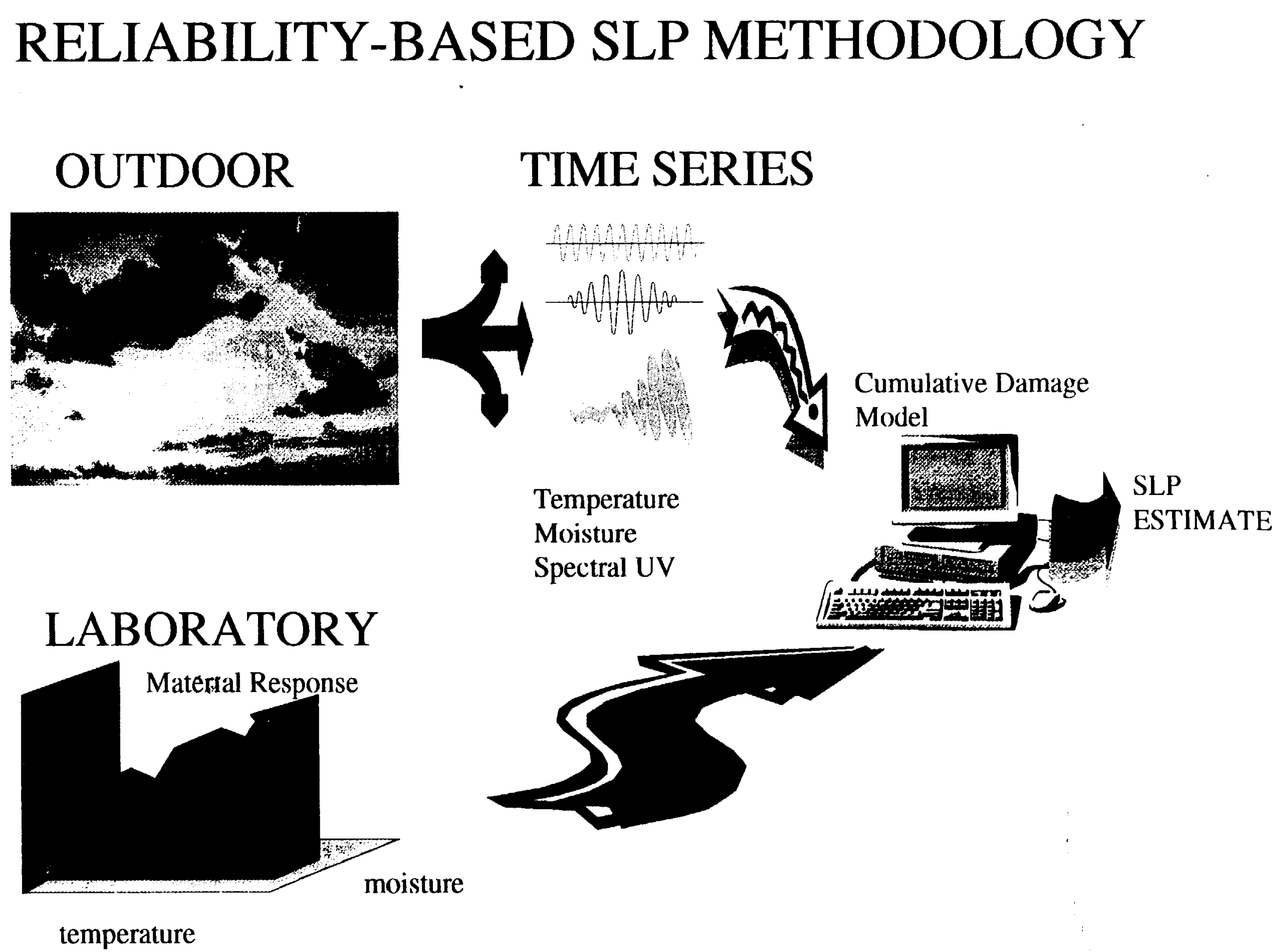


Figure 2—Schematic depicting the test strategy for the reliability-based service life prediction methodology.

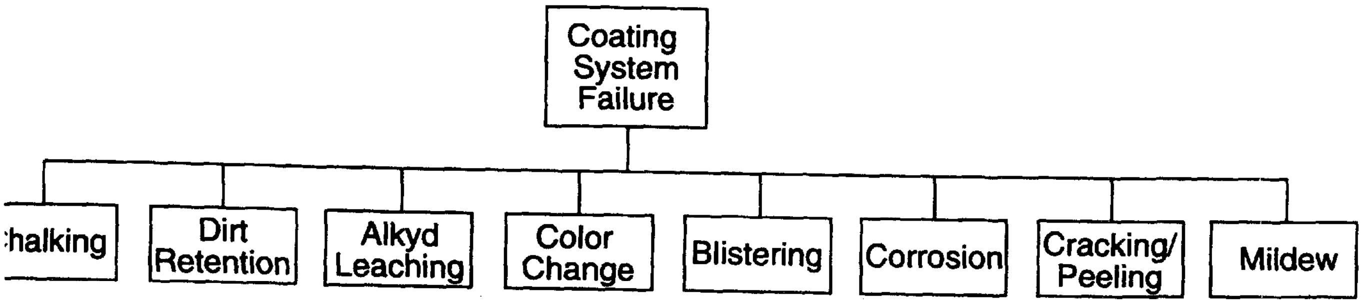


Figure 3—Common loss of protection and loss of appearance failure modes for coating systems.

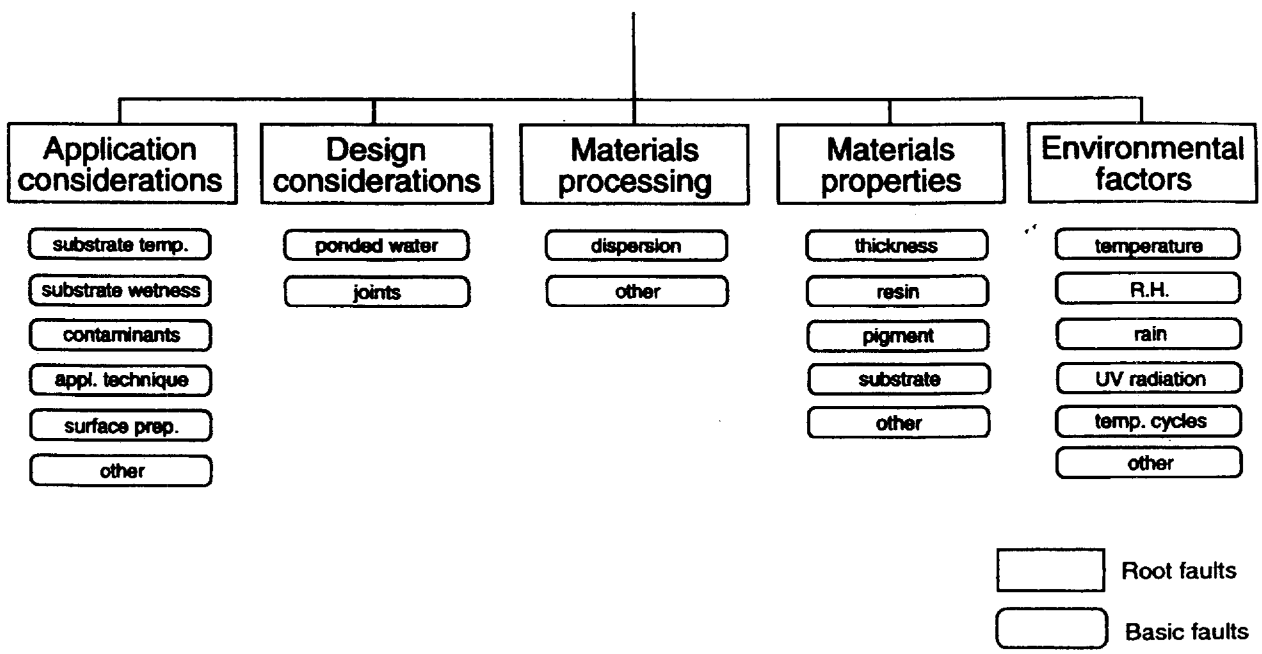


Figure 4—Common root and basic faults associated with the failure of maintenance coatings.

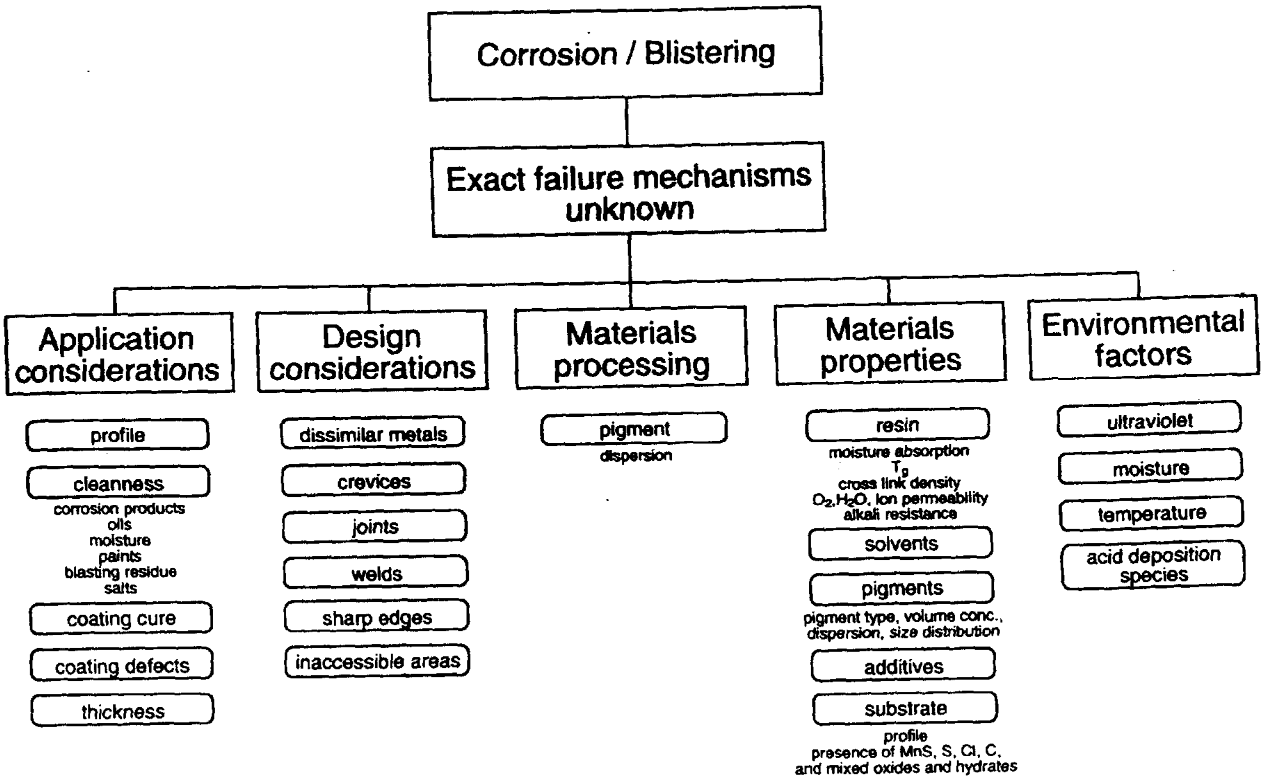


Figure 5—Fault tree for loss of protection due to corrosion where the underlying failure mechanisms are poorly understood. This lack of understanding is graphically portrayed by the black box between the observed failure mode and the root faults.

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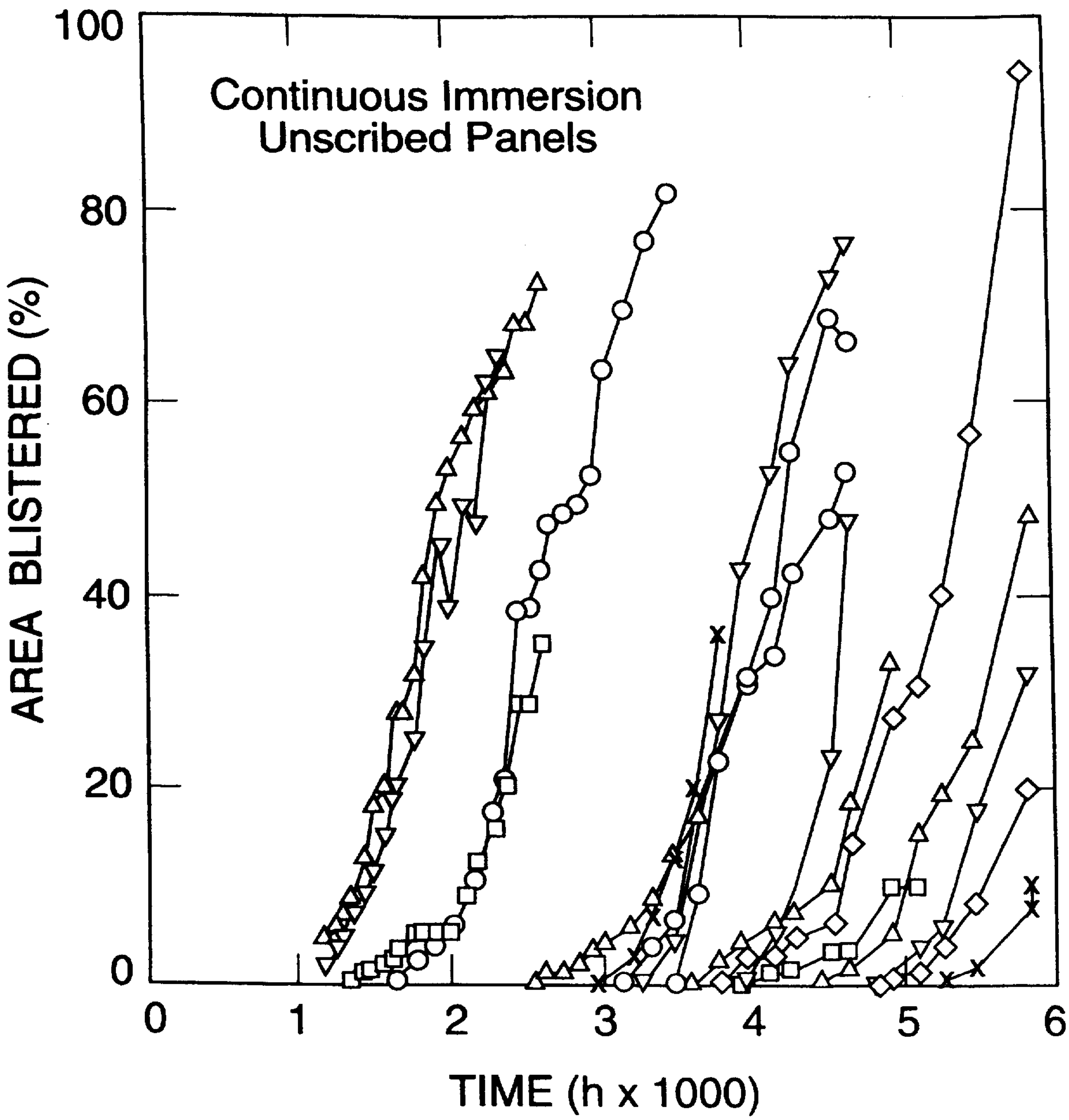

Figure 7—Percent area blisters versus immersion time for 24 nominally identical and simultaneously immersed coated steel panels containing no intentionally induced defects. The panels were continuously immersed in 5% NaCl solution. Six of the 24 panels displayed no degradation after 6000 h of immersion (taken from Martin et al. 1990).

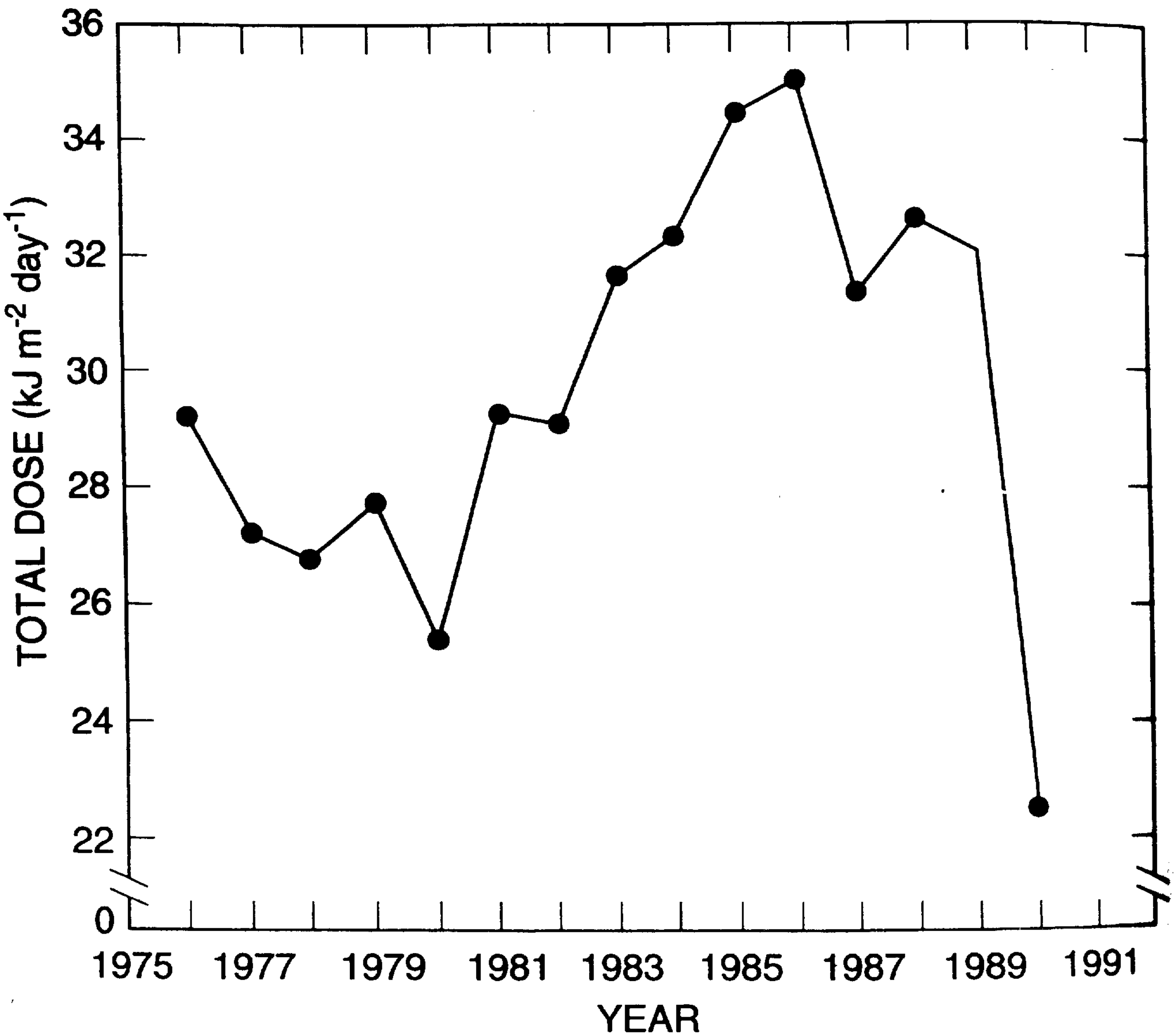

Figure 8—Time series of the calendar-year average of total average daily UVB radiation dosage from 1975 to 1990 in Rockville, MD (taken from Correll et al., 1992).